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(54) Preparation of rubber composition by aqueous elastomer emulsion mixing and articles thereof including tires

(57) The invention relates to preparation of a rubber composition by pre-mixing at least one rubber compounding ingredient with an aqueous emulsion, or latex, of at least one elastomer. The invention also contemplates the use of such rubber composition, or blend of such rubber composition with at least one additional elastomer and/or rubber compounding ingredient, as a component of an article of manufacture. Such article of manufacture may be, for example, a tire. Such article may also be an industrial product such as a hose or belt such as a conveyor belt or power transmission belt.

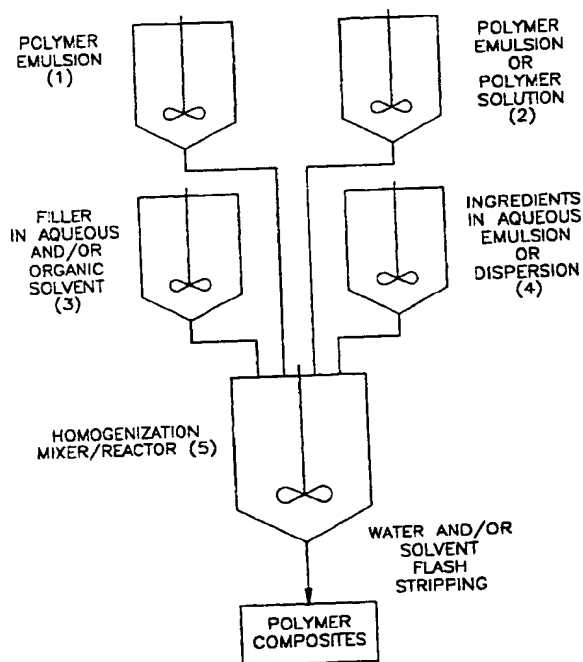
POLYMER COMPOSITES FROM AQUEOUS  
EMULSION/DISPERSION MIXING

FIG-1

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## Description

### Field of the Invention

[0001] This invention relates to preparation of a rubber composition by pre-mixing at least one rubber compounding ingredient with an aqueous emulsion, or latex, of at least one elastomer. The invention also contemplates the use of such rubber composition, or a blend of such rubber composition with additional elastomer(s) and/or rubber compounding ingredients, as a component of an article of manufacture. Such article of manufacture may be, for example, a tire. Such article may also be an industrial product such as, for example, a hose or belt such as a conveyor belt or power transmission belt.

### Background of the Invention

[0002] Various rubber compounding ingredients, including particulate carbon black reinforcement, are conventionally blended with various elastomers with the aid of various internal mixers, as well as open roll mixers, under high shear and relative high temperature conditions. Accordingly a considerable amount stress is experienced by the rubber composition as well as expenditure of energy to accomplish the aforesaid mixing.

[0003] Alternatively, various rubber compositions have heretofore been prepared by:

- (1) first masterbatching various aqueous rubber emulsions, or latices, with various rubber compounding ingredients which have particularly included rubber reinforcing carbon black under low shear and temperatures followed by
- (2) blending the masterbatch with additional elastomer(s) and compounding ingredients under high shear and temperature conditions.

[0004] For example, see US-A- 3,294,733; 3,298,984; 3,317,458; 3,345,324; 3,491,052; 3,767,605 and 3,923,707.

[0005] US-A- 3,317,458, for example, relates to masterbatching a combination of carbon black and silica with a rubber latex.

[0006] Various rubber compositions have also heretofore been prepared by mixing an aqueous slurry of carbon black with an organic solvent solution of elastomer(s). For example see US-A- 3,350,342.

[0007] US-A- 3,304,281 relates to mixing together a solution of one polymer with a latex of another polymer and then coagulating the rubber crumb from the resulting mixture. The process can be used to incorporate an oil and/or carbon black into the polymer. For example, the oil can be introduced as an aqueous emulsion and the oil emulsion mixed with the latex prior to contact with the solution. Alternatively, all three components can be mixed simultaneously. Alternatively, a carbon black aqueous slurry can be added to the solution-latex mix-

ture or it can be mixed with the latex prior to mixing with the solution.

[0008] US-A- 3,491,052 relates to mixing an elastomer in an aqueous latex form with a solution of an elastomer which has been dissolved in a water immiscible organic solvent to form a pseudo-emulsion and recovering the mixed elastomers by adding a latex coagulating agent at a temperature sufficient to vaporize the solvent. Alternatively a rubber pigment (e.g.: carbon black) may be dispersed in the pseudo-emulsion prior to coagulation.

[0009] US-A- 3,533,988, for example, relates to blending a hydrocarbon solution of rubber with an aqueous suspension of a rubber reinforcing agent, such as carbon black. In its background discussion, it relates that, theretofore, in order to avoid a disagreeableness of handling dry, dusty carbon black with raw rubber on mixing rolls, a method was developed for producing masterbatch by dispersing carbon black directly into a rubber solution produced by monomer polymerization in the presence of a solvent. It further relates that, theretofore, another method was to disperse carbon black in a hydrocarbon and mix the dispersion with the rubber solution.

[0010] In the description of this invention, the term "phr" relates to parts by weight of an ingredient per 100 parts by weight of rubber.

[0011] The terms "rubber" and "elastomer" are used interchangeably unless otherwise specified.

[0012] The term "Tg" relates to a glass transition temperature of an elastomer, normally determined by a differential scanning (DSC) calorimeter with a temperature rise of 10 °C per minute.

### Disclosure and Practice of the Invention

[0013] In accordance with this invention, a process of preparing a rubber composition is provided which comprises:

- (A) blending a particulate elastomer-reinforcing filler and at least one additional rubber compounding ingredient with an aqueous emulsion of a conjugated diene-based elastomer solution and recovering a composition thereof by removing the water therefrom wherein said filler and compounding ingredient (s) are blended with said latex therewith in a form of:

#### (1) particulate

- (a) elastomer-reinforcing filler exclusive of aqueous or organic dispersion of said filler and
- (b) at least one additional rubber compounding ingredient,

#### (2) particulate

- (a) elastomer-reinforcing filler as a dispersion thereof in an organic solvent and
- (b) at least one additional rubber compounding ingredient, and/or

(3) particulate

- (a) elastomer-reinforcing filler as a dispersion thereof in water and
- (b) at least one additional rubber compounding ingredient, or

(B) spraying an aqueous emulsion of a conjugated diene-based elastomer onto

- (1) a particulate elastomer-reinforcing filler and
- (2) at least one additional rubber compounding ingredient, and recovering a composition thereof by removing the water therefrom;

wherein said reinforcing filler is selected from at least one of carbon black, synthetic amorphous silica, particularly precipitated silica aggregates and fumed silica, carbon black and modified carbon black having domains of silica on the surface thereof, and

wherein said additional rubber compounding ingredient is selected from at least one of:

- (A) additional diene-based elastomers(s);
- (B) zinc oxide;
- (C) sulfur;
- (D) vulcanization accelerator(s);
- (E) microcrystalline and paraffin waxes;
- (F) antidegradants; and
- (G) vulcanization retarders.

[0014] In practice, said aqueous emulsion of said elastomer may be a polymerizate.

[0015] In additional accordance with this invention, a preferred carbon black and silica have a relatively low apparent density prior to said blending in a range of 3 to 300, alternatively 3 to 140 g/l. This low density is substantially lower than conventional carbon blacks and silicas, which more conventionally have an apparent density in a range of 500 to 1000 g/l.

[0016] Exemplary of more conventional silicas are precipitated silicas and exemplary of conventional carbon blacks are those in which the carbon black powder has been processed to form very small pellets and which have designations such as N234, N121, N330, etc which are ASTM designations.

[0017] Exemplary of silicas and carbon blacks with the said low apparent densities are, for example, fumed silicas and fine carbon black powders prior to their pelletization to form the said N234, N122 and N330 (for example) designated carbon blacks. Such fine carbon black powders are not normally used for rubber reinforcement purposes, although carbon blacks in the

aforesaid pelletized form, with attendant higher apparent densities, are conventionally used for rubber reinforcement purposes.

[0018] A significant aspect of using the silica and carbon black powder with very low apparent densities for this invention is to utilize the high absorption capacities of such reinforcing fillers, particularly where it is desired for the reinforcing filler to have a greater ability to absorb various rubber compounding ingredients onto its surface and to thereby ultimately provide a resulting free flowing rubber composition.

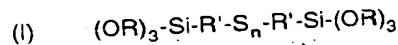
[0019] As previously presented, the process of this invention may involve spraying said aqueous emulsion of diene-based elastomer (latex) onto said particulate reinforcing filler and additional rubber compounding ingredient(s).

[0020] As a feature of said spraying process, said particulate filler and additional compounding ingredient(s) are preferably agitated during said spraying of said latex.

[0021] As an additional feature of said spraying process, the aqueous emulsion of said elastomer(s) is substantially dried upon said particulate reinforcing filler and additional compounding ingredient(s) as it is being agitated.

[0022] In additional accordance with this invention, said suspension, or dispersion, of said reinforcing filler, additional compounding ingredient(s) and said aqueous emulsion of elastomer(s) is heat treated by heating the mixture, while agitating the mixture, to a temperature within a range of 30°C to 150°C, alternatively 40°C to 150°C, for 2 to 30, alternatively 3 to 20 minutes prior to drying the said composite. If appropriate, the mixture may need to be contained under pressure in a suitable container or under reflux conditions where evaporating water is returned to the mixture during the heat treatment operation.

[0023] In further accordance with this invention, the silica is an amorphous silica which is pre-treated, prior blending with said organic solvent solution of elastomer(s), by reacting said silica, preferably a precipitated silica, with an organosilane selected from at least one of the general formulas (I) and (II):



wherein R is the same or different alkyl radical selected from at least one of ethyl and methyl radicals, preferably the same radicals and preferably an ethyl radical; R' is the same or different radical selected from at least one of ethyl, propyl and butyl radicals, preferably the same radical and preferably a propyl radical; and n is a value from 2 to 6 with an average of from 2 to 2.6 or from 3.5 to 4 and Z is independently selected from -SH, -NH<sub>2</sub>,

Acrylat, R'-NH-R', epoxy, -SCN, -NCO, -Sn-NH-R'-Si(OR)<sub>3</sub> groups.

[0024] Thus, such organosilane may be, for example, a bis-(3-alkoxysilylalkyl) polysulfide with an average of from 2 to 2.6 or from 3.5 to 4 connecting sulfur atoms in its polysulfidic bridge. Representative thereof is a bis (3-ethoxysilylpropyl) polysulfide.

[0025] In one aspect of the invention, said aqueous emulsion of elastomer(s) may be composed of at a multiplicity of least two individual aqueous emulsions of elastomers

(A) which are pre-blended prior to addition of said reinforcing filler(s) and additional compounding ingredient, or

(B) which at least one of said of elastomer aqueous emulsions is blended with at least one additional elastomer aqueous emulsion subsequent to said reinforcing filler and additional compounding ingredient addition thereto or

(C) which at least one of said elastomer aqueous emulsions is blended with at least one additional elastomer aqueous emulsion substantially simultaneously with said reinforcing filler and additional compounding ingredient addition.

[0026] In one aspect of the invention, at least one of said aqueous elastomer emulsions may be a polymerizate (an elastomer contained in the aqueous emulsion in which its precursor monomers are polymerized, or copolymerized as the case may be for the preparation of the elastomer).

[0027] In practice, said polymerizate may be a polymerizate in which the polymerization reaction has not been terminated and which may be referred to as a living polymer, or polymerizate. In such case, it is envisioned that, as the polymerization continues, the polymer may interact with the reinforcing filler to create an improved, or more efficient and integral dispersion of the filler within the elastomer host.

[0028] For the aforesaid process steps (A) and (B) of this invention, at least one of said additional rubber compounding ingredients is blended with said aqueous emulsion of said elastomer(s), and/or an emulsion of said rubber composition, and/or an emulsion of said rubber composition dissolved (dispersed) in solvent, which may be before, substantially simultaneously with, or subsequent to, said reinforcing filler addition, which is comprised of at least one of:

(A) microcrystalline and paraffin waxes in a range of 0.1 to 10 phr;

(B) antioxidant(s) selected from amine-based and phenolic-based antioxidants in a range of 0.1 to 10 phr;

(C) sulfur vulcanization accelerator(s) in a range of 0.1 to 10 phr;

(D) sulfur vulcanization retarder(s) in a range of

0.01 to 5 phr;

(E) sulfur vulcanization activator(s) in a range of 0.1 to 10 phr;

(F) rubber processing oil(s) selected from at least one of aromatic, paraffinic and naphthenic rubber processing oils in a range of 1 to 60 phr; and

(G) sulfur in an amount of 0.1 to 3 phr.

[0029] Microcrystalline waxes are well known waxes for use in rubber compositions. Such waxes are defined by The Condensed Chemical Dictionary, Ninth Edition (1970), Page 925, as "A wax, usually branched-chain paraffins, characterized by a crystal structure much smaller than that of normal wax and also by much higher viscosity".

[0030] Representative of commercial microcrystalline waxes are, for example, those available as Akrowax from the Akrochem Company; as an Antilux series of waxes from the Rein Chemie Company; as "Be-Square" 175 Amber Wax from the Petrolite Company; as Beesyn White Wax from the International Wax Company; and as an Okerin series of waxes from the Astor-Wax Company.

[0031] Representative examples of antioxidants are amine-based and phenolic based antidegradants. Representative of various commercially available antidegradants may be found, for example in the 1997 Blue Book published by Rubber World, a Lippincott & Peto Publication, Pages 132 through 168.

[0032] Representative of such commercially available antidegradants are, for example, diphenyl-p-phenylenediamine as AgeRite DPPD from the R. T. Vanderbilt Company and octylated diphenyl amines such as AgeRite Statlite from the R. T. Vanderbilt Company.

[0033] Additional antidegradants are for example, 2,5-D-t-dibutylhydroquinone, N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine, polymerized 1,2-dihydro-2,2,4-trimethylquinoline, diaryl-p-phenylene diamine, 4,4'-methylene bis 2,6 di tert butylphenol, N, N'-di-3 (5-methylheptyl)-p-phenylenediamine, 2,2-methylene-bis(4-methyl-6-tert-butyl phenol), 4,4'-dicumyldiphenylamine, and N-cyclohexylthiophthalimide.

[0034] Representative examples of various sulfur vulcanization accelerators are those found in The Vanderbilt Rubber Handbook (1978), Pages 354 through 383, and in the 1977 Blue Book, infra, Pages 17 through 74.

[0035] Representative of commercial sulfur vulcanization accelerators are, for example dibenzothiazyl disulfide as Altex from the Elastochem Company; 2-mercaptobenzothiazole as Captax from the Elastochem Company; N-oxydiethylene benzothiazole-2-sulfenamide as Amax from the R.T. Vanderbilt Company; 4-morpholinyl-2-benzothiazole disulfide as Morfax from the R.T. Vanderbilt Company; tetramethylthiuram disulfid as M thyl Tuads from the Elastochem Company; and tetramethylthiuram monosulfide as Unads from the Elastochem Company.

[0036] Additional vulcanization accelerators are, for

example, tetrabutylthiuram disulfide, zinc dibutyldithiocarbamate, thiocarbonylsulfenamide, N-cyclohexyl-2-benzothiazolesulfenamide, N-t-butyl-2-benzothiazole sulfenamide, and diphenylguanidine.

[0037] Representative examples of various vulcanization retarders are those found in The Vanderbilt Rubber Handbook (1978), *infra*, Page 403 and in the "1977 Blue Book", *infra*, Pages 98 through 102.

[0038] Representative of commercial vulcanization retarders is, for example, N-nitrosodiphenylamine from the Sovereign Chemical Company as well as N-cyclohexyl thiophthalimide, magnesium oxide, and N-(cyclohexylthio)-phthalimide.

[0039] Representative examples of various vulcanization activators are those found in the "1977 Blue Book", *infra*, Pages 75 through 97.

[0040] Representative of commercial vulcanization activators are, for example, zinc oxide from the Akrochem Company and stearic acid-rubber grade from the Akrochem Company.

[0041] Representative examples of various plasticizers and softeners are those found in the 1977 Blue Book, *infra*, Pages 179 through 216.

[0042] Representative examples of various vulcanizers are those found in the 1977 Blue Book, *infra*, Pages 102 through 128.

[0043] Representative of commercial vulcanizers is, for example, sulfur in its different forms as native or alpha-sulfur (S8) and/or as insoluble sulfur with or without treatment from the Akrochem Company.

[0044] In additional accordance with the process of this invention, particularly where said additional compounding ingredients added to the elastomer emulsion include zinc oxide, stearic acid, and sulfur, process step (C) is provided which comprises sulfur vulcanizing said recovered rubber composite at a temperature in a range of 120°C to 180°C, preferably from 140°C to 180°C for 2 to 120 minutes, preferably from 7 to 30 minutes depending on the temperature selected and tire type.

[0045] In further accordance with the process of this invention, the resultant rubber composition is blended with at least one additional diene-based elastomer and/or compounding ingredient then sulfur vulcanized.

[0046] In additional accordance with the process of this invention, an article of manufacture is prepared having at least one component of the rubber composition of this invention or as blend with at least one additional elastomer and/or compounding ingredient.

[0047] In practice, the article of manufacture of this invention may be, for example, a tire or an industrial product such as, for example a hose or belt such as, for example a conveyor belt or power transmission belt.

[0048] In additional accordance with this invention a tire is provided having a component of the rubber composition prepared according with this invention. In additional accordance with this invention a tire is provided having a tread of the rubber composition prepared according with this invention.

[0049] It is a significant aspect of this invention that the diene-based elastomer(s) together with one or more of zinc oxide, sulfur, vulcanization accelerator(s) and reinforcing filler may be all mixed together under controlled shear and controlled temperature conditions without being limited by the conventional high shear mixing accompanied by largely uncontrollable, autogenous, temperature increase as experienced in classical internal rubber mixers. This aspect is considered herein as being novel and significant because

(A) the polymer in its aqueous emulsion state is at a very high, and possibly its highest possible, dispersion state; and

(B) various additional compounding ingredients, including particulate reinforcing fillers, particularly said carbon black powder and fumed silica with their aforesaid low apparent densities are also at a very high, and perhaps their highest, dispersion state, namely, as a solution, or dispersion, thereof in an aqueous medium.

[0050] Particular benefits of the process of this invention are considered herein to be:

(A) A relative minimal amount of additional energy is needed for polymer drying in a case where the polymer is adsorbed onto the filler or the polymer is mixed with the filler.

(B) No additional energy or process step is needed for pelletization of carbon black fillers prior to mixing with the elastomer, namely pellets for carbon black, and granules or small spheres for precipitated silica, especially where the aforesaid carbon black powders, as well as fumed silica, with their low apparent densities are used.

(C) The use of fumed silicas with very low apparent density (ASTM-D1513) may be enabled because such silicas may absorb the water of the emulsion, thereby transforming the highly dusting silica (due to the silica's low apparent density) to a compacted and more usable material.

(D) Concerns about flaking or pearling of various ingredients to be mixed with the elastomer should be minimized because the ingredients will be dissolved, or more typically dispersed, in the water of the aqueous emulsion and therefore there is no need for a specific physical dry mixing of the utilized ingredients.

(E) Only a relative minimal energy would normally be necessary for dispersing various compounding ingredients in the elastomer because the mixing of specified ingredients will be reduced to a blending of emulsions.

(F) An increased uniformity of dispersion of various compounding ingredients, including particulate reinforcing fillers, particularly where such fillers may be hydrophobic in nature, in the elastomer because

such materials, as a solution or more likely a dispersion in the water of the aqueous emulsion, will be in their most dispersible state and because the blending/mixing in the aqueous emulsion has the highest dispersion/blending and homogenizing capability as compared to dry blending the ingredients.

(G) A reduction in amounts of various compounding ingredients needed for the rubber composition formulation is expected because of better anticipated dispersion of a respective compounding ingredients within the elastomer due to emulsion blending as compared to dry blending of the ingredients.

(H) Better resistance to abrasion is expected for the resulting vulcanized rubber composition which contains particulate amorphous silica for its reinforcement and which has been blended with the elastomer by water emulsion mixing.

(I) Better control of various chemical reactions which typically occur during the mixing of various ingredients is expected where solution, emulsion mixing of the associated ingredients is utilized as compared to simple dry mixing of the ingredients under high shear and elevated temperature mixing in an internal rubber mixer.

[0051] As hereinbefore discussed, in further practice of the invention, said diene-based elastomer may be provided in a form of an aqueous polymerizate emulsion of such elastomer.

[0052] Indeed, one significant aspect of this invention is a utilization of an aqueous polymerizate emulsion of the elastomer instead of re-dissolving the elastomer in a volatile organic solvent.

[0053] In additional practice of this invention, the rubber composition prepared by the process of the aforesaid steps (A) and (B) may be in a form of a pre-formed rubber composition, or composite, which is subsequently mixed under high shear and temperature conditions with at least one additional compounding ingredient comprised of at least one of

- (A) additional diene-based elastomer(s);
- (B) zinc oxide;
- (C) sulfur;
- (D) vulcanization accelerator(s);
- (E) microcrystalline waxes;
- (F) antidegradants; and
- (G) particulate reinforcing filler(s).

[0054] In practice, it may be preferable for a particulate reinforcing filler to be mixed with the elastomer solution, including fillers such as, for example fumed silica, modified carbon black having domains of silica on the surface thereof and carbon blacks, to have relatively small apparent densities (ASTM method D-1513) within a range of 10 g/l to 300 g/l.

[0055] The preference toward relatively small appar-

ent densities for the reinforcing filler(s) is for the fillers to more homogeneously disperse within the aqueous emulsion and, ultimately, to disperse more homogeneously within the elastomer itself.

[0056] A preference herein toward use of relatively low apparent densities for the reinforcing fillers is to utilize the high absorption capacities of such fillers, particularly where it is desired for the filler to have a greater ability to absorb various ingredients onto its surface and to thereby ultimately provide a resulting free flowing rubber composition. For example, the concentration of such filler in the aqueous elastomer emulsion may be adjusted so that the water may be more readily absorbed by the filler thereby generating a compact composite with acceptable processing properties, namely, to squeeze out the water in an extruder or between mill rolls without having to evaporate the water, thus representing a substantial saving in energy and process complexity resulting in a material to form bales thereof.

[0057] In practice, it is often desired that the reinforcing filler is carbon black. While the various conventional, pelletized rubber reinforcing carbon blacks might be used, it is, as hereinbefore discussed, preferred to use an un-pelletized carbon black powder having a relatively low apparent density (ASTM method D-1513) before mixing with the elastomer in a range of 3 to 140, alternately 3 to 300, g/l. Representative of conventional pelletized carbon blacks having higher apparent densities, as hereinbefore discussed, for example, the various N-series of carbon blacks referenced in The Vanderbilt Rubber Handbook, 13th Edition, 1990, Page 417. It is to be appreciated that desirable carbon black powders for use in this invention are carbon black powders prior to pelletization to form said conventional pelletized carbon blacks.

[0058] In practice, it may be desired to use fumed silica with its aforesaid low apparent density.

[0059] However, it may sometimes be desired to use silicas with the aforesaid higher apparent density such as for example precipitated aluminosilicates, may be used it may sometimes be preferred to use a silica having a relatively high apparent density (ASTM method D-1513) in a range, for example, of 500 g/l to 1000 g/l for mixing with the elastomer solution as hereinbefore discussed. Representative of contemplated precipitated silicas are, for example, RP120HD, RP85, Z85MP, Z1165MP, RP240HD and RP200MP from Rhodia; VN2, VN3, and Vetrasil 7000 from Degussa A.G.; Hi-sil 532 from PPG Industries; Zeopol 8745 and 8755 from Huber; Perkasil 233 from Akzo.

[0060] As hereinbefore discussed, it may sometimes be desired to use, as a reinforcing filler, a silica treated carbon black having domains of silica on the surface thereof.

[0061] In the practice of the invention, various sulfur vulcanizable elastomers may be used, exemplary of which are homopolymers and copolymers of conjugated diene hydrocarbons and copolymers of at least one con-

jugated diene hydrocarbon with an aromatic vinyl compound selected from styrene and alpha-methyl styrene.

[0062] Preferred conjugated dienes are isoprene and 1,3-butadiene. Preferred aromatic vinyl compound is styrene.

[0063] Representative of various conjugated diene-based elastomers are, for example, cis 1,4-polyisoprene, 1,3-butadiene, styrene/butadiene copolymers, isoprene/butadiene copolymers, styrene/isoprene/butadiene copolymers and any functionalized versions of them.

[0064] Preferably, such conjugated diene-based elastomers are prepared by emulsion and/or solvent solution polymerization. In such case, such elastomers may be preferably used in their polymerize form as hereinbefore discussed, namely in the aqueous emulsion state prior to coagulation in their monomers are polymerized to form the elastomer, so that the elastomers do not have to be re-dispersed in water.

[0065] The rubber composition prepared by the process of this invention is considered herein as being useful, or advantageous, in the preparation of rubber composition as a component of an article of manufacture, instead of dry-blending, or in combination with dry blending, rubber compounding ingredients with rubber because the expected improved dispersion of dispersed ingredients within the elastomer, including reinforcing fillers; expected improved uniformity of dispersion of respective ingredients within the elastomer; improved energy balance because the typical very high energy needed to dry mixing the ingredients in an internal rubber mixer is replaced by a low energy aqueous emulsion mixing/blending process; more efficient use of respective compounding ingredients within the elastomer, including a reduction of quantity; improved efficiency of mixing ingredients within an elastomer and therefore improved overall manufacturing efficiency.

[0066] As hereinbefore discussed, rubber compositions for this invention may also be prepared by mixing the rubber composition, or composite, prepared by aforesaid processes (A) and (B) with various sulfur vulcanizable elastomers and/or additional rubber compounding ingredients by compounding by methods generally known in the rubber compounding art, such as mixing in an internal rubber mixer with various commonly used additive materials such as, for example, curing aids, such as sulfur, activators, retarders and accelerators; processing additives, such as oils, resins including tackifying resins, silicas, and plasticizers, fillers, pigments, fatty acid, zinc oxide, waxes, antioxidants and antiozonants, peptizing agents and reinforcing materials such as, for example, carbon black. As known to those skilled in the art, depending on the intended use of the sulfur vulcanizable and sulfur vulcanized material (rubbers), the additives mentioned above are selected and commonly used in conventional amounts.

[0067] Typical amounts of tackifier resins, if used, may comprise 0.5 to 10 phr, usually 1 to 5 phr. Typical

amounts of processing aids may comprise 1 to 10 phr, if used. Such processing aids can include, for example, aromatic, naphthenic, and/or paraffinic processing oils. Representative silicas may be, for example, hydrated amorphous silicas. Typical amounts of antioxidants comprise 1 to 3 phr. Representative antioxidants may be, for example, diphenyl-p-phenylenediamine and others, such as, for example, those disclosed in The Vanderbilt Rubber Handbook (1978), Pages 344 through 346. Typical amounts of antiozonants for the sidewall composition may comprise 3 to 6 phr. Typical amounts of fatty acids, if used, which can include stearic acid comprise 0.5 to 3 phr. Typical amounts of zinc oxide comprise 2 to 6 phr. Typical amounts of waxes comprise 1 to 5 phr. Often microcrystalline waxes are used. Typical amounts of peptizers comprise 0.1 to 1 phr. Typical peptizers may be, for example, pentachlorothiophenol and dibenzamidodiphenyl disulfide.

[0068] The presence and relative amounts of the above additives are considered to be not an aspect of the present invention which is more primarily directed to the masterbatch preparation, in an aqueous suspension/emulsion, of a pre-formed composite and the further preparation and use of rubber compositions which contain such pre-formed composite.

[0069] The vulcanization is conducted in the presence of a sulfur vulcanizing agent. Examples of suitable sulfur vulcanizing agents include elemental sulfur (free sulfur) or sulfur donating vulcanizing agents, for example, an amine disulfide, polymeric polysulfide or sulfur olefin adducts. Preferably, the sulfur vulcanizing agent is elemental sulfur. As known to those skilled in the art, sulfur vulcanizing agents are used in an amount ranging from 0.5 to 4 phr, with a range of from 0.5 to 2.5 phr being preferred.

[0070] Accelerators, including primary and optionally secondary accelerators, are used to control the time and/or temperature required for vulcanization and to improve the properties of the vulcanizate. Often accelerators are used in an amount ranging from 0.5 to 2.0 phr. Such accelerators may be, for example, various amines, disulfides, guanidines, thioureas, thiazoles, thiurams, sulfenamides, dithiocarbamates and xanthates. Preferably, the primary accelerator is a sulfenamide. If a second accelerator is used, the secondary accelerator is preferably a guanidine, dithiocarbamate or thiuram compound.

[0071] Sometimes a combination of antioxidants, antiozonants and waxes may be collectively referred to as "antidegradants".

[0072] The presence and relative amounts of the respective compounding ingredients are not necessarily considered to be an aspect of this invention, except where noted, and except that a practice of this invention is expected to result in a more efficient use of some of the ingredients, as hereinbefore discussed, which may result, in some cases, in a reduction on amounts of use of some ingredients.

[0073] A tire can be built, shaped, molded and cured by various methods, which will be readily apparent to those having skill in such art.

[0074] The prepared tire of this invention is conventionally shaped and cured by methods known to those having skill in such art.

[0075] For further illustration of the invention, the following drawings are presented which are not intended to be limiting as to the invention.

[0076] FIG 1 is a schematic diagram of emulsion preparation of an elastomer composite, which is entitled "Polymer Composites From Emulsion Mixing".

[0077] In particular, with reference to FIG 1, a polymer emulsion (1) and, optionally, a polymer emulsion (2), a polymer solution (2') is fed from its (their) respective associated container(s), within which may be an agitated solution, to an homogenization mixer (5). It is to be appreciated that the polymer emulsion (1), polymer emulsion (2), and/or polymer solution (2') may be a polymerizate.

[0078] In addition, a filler (3) such as carbon black powder with a low apparent density in a range of 3 to 140 g/l, and optionally in an aqueous or/and organic solvent dispersion thereof, is fed from its associated container, within which it may be agitated, to said homogenization mixer (5) and thereby mixed with said polymer (s) (1) and/or (2) and/or (2').

[0079] Further, ingredient(s) (4), such as for example, zinc oxide, stearic acid, sulfur and vulcanization accelerator(s) may be fed from its (their) respective container, preferably in an aqueous emulsion /dispersion within which it (they) may be agitated, to said homogenization mixer/reactor (5) and thereby mixed with said elastomer (s) (1) and/or (2) and/or (2') and said filler (3).

[0080] Thereafter, the mixture is removed from said homogenization mixer, and coagulated to yield masterbatch composite precipitated, that might be separated from the liquid phase by sedimentation, filtration, centrifugation or extrusion to recover the polymer composite(s). Washing steps might also be added depending somewhat on the purity level desired. These operations might be repeated as often as required. This composite can be dried by flush drying, vacuum drying, hot extrusion drying, eliminating the residual water and solvent, if any, as depicted in the FIG 1.

[0081] In practice, the recovered polymer composite may be used as a component of an article of manufacture such as, for example, a component of a tire and/or industrial product. Such tire component may be, for example and without limitation, a tire tread, sidewall, apex or other sidewall insert, or wire coat compound. Such industrial product may be, for example and without limitation, a hose, conveyor belt or power transmission belt.

## Claims

1. A process of preparing a rubber composition char-

acterized by comprising:

(A) blending a particulate elastomer-reinforcing filler and at least one additional rubber compounding ingredient with an aqueous emulsion of a conjugated diene-based elastomer solution and recovering a composition thereof by removing the water therefrom wherein said filler and compounding ingredient(s) are blended with said latex therewith in a form of:

(1) particulate

- (a) elastomer-reinforcing filler exclusive of aqueous or organic dispersion of said filler and
- (b) at least one additional rubber compounding ingredient;

(2) particulate

- (a) elastomer-reinforcing filler as a dispersion thereof in an organic solvent and
- (b) at least one additional rubber compounding ingredient; and/or

(3) particulate

- (a) elastomer-reinforcing filler as a dispersion thereof in water and
- (b) at least one additional rubber compounding ingredient; or

(B) spraying an aqueous emulsion of a conjugated diene-based elastomer onto

- (1) a particulate elastomer-reinforcing filler and
- (2) at least one additional rubber compounding ingredient; and recovering a composition thereof by removing the water therefrom;

wherein said reinforcing filler is selected from at least one of carbon black, synthetic amorphous silica particularly precipitated silica aggregates and fumed silica, carbon black and modified carbon black having domains of silica on the surface thereof, and

wherein said additional rubber compounding ingredient is selected from at least one of

- (A) additional diene-based elastomer(s);
- (B) zinc oxide;
- (C) sulfur;
- (D) vulcanization accelerator(s);
- (E) microcrystalline and paraffin waxes;

- (F) antidegradants; and  
(G) vulcanization retarders.

2. The process of claim 1 **characterized by** comprising blending at least one particulate, elastomer reinforcing filler and at least one additional rubber compounding ingredient; of aqueous or organic solvent dispersion of said filler, with an aqueous emulsion of at least one diene-based elastomer to form a suspension, or dispersion, of said filler in said elastomer emulsion, followed by recovering said blend as an elastomer composite by removing water therefrom.

3. The process of claim 1 **characterized in that** said blending process is a spray-blending process which comprises

(A) spraying said aqueous emulsion of at least one diene-based elastomer onto said particulate reinforcing filler and the at least one additional rubber compounding ingredient and wherein said aqueous emulsion of said elastomer(s) is substantially dried upon said particulate reinforcing filler and said at least one additional rubber compounding ingredient as it is being agitated as a suspension or dispersion thereof; or

(B) the spray-blending process of (A) wherein said suspension, or dispersion, of said reinforcing filler, at least one additional rubber compounding ingredient and said aqueous emulsion of elastomer(s) is heat treated by heating the mixture, while agitating the mixture, to a temperature within a range of 30°C to 150°C for 2 to 30 minutes prior to drying the said composite.

4. The process of any of the preceding claims **characterized in that** said particulate reinforcing filler is comprised of at least one of carbon black, amorphous precipitated silica aggregates, and modified carbon black having silica domains on its surface.

5. The process of claim 1 **characterized in that** an additional ingredient is blended with said elastomer emulsion, wherein said additional ingredient is selected from at least one of, based upon 100 parts by weight elastomer (phr):

(A) microcrystalline waxes in a range of 0.1 to 10 phr;

(B) antioxidant(s) selected from amine-based and phenolic-based antioxidants in a range of 0.1 to 10 phr;

(C) sulfur vulcanization accelerator(s) in a range of 0.1 to 10 phr;

(D) sulfur vulcanization retarder(s) in a range

of 0.01 to 5 phr;

(E) sulfur vulcanization activator(s) in a range of 0.1 to 10 phr;

(F) rubber processing oil(s) selected from at least one of aromatic, paraffinic and naphthenic rubber processing oils in a range of 1 to 60 phr; and

(G) sulfur in an amount of 0.1 to 3 phr.

6. The process of claim 1 **characterized in that** an additional ingredient is blended with said elastomer emulsion, wherein said additional ingredient is selected from

(A) an antidegradant is selected from at least one of diphenyl-p-phenylene-diamine, octylated diphenyl amine, 2,5-D-t-dibutylhydroquinone, N-1,3-dimethylbutyl-N'-phenyl-p-phenylenediamine, polymerized 1,2-dihydro-2,2,4-trimethylquinoline, diaryl-p-phenylene diamine, 4,4'-methylene bis 2,6 di tert butylphenol, N,N'-di-3(5-methylheptyl)-p-phenylenediamine, 2,2-methylene-bis(4-methyl-6-t-butylphenol), 4,4'-dicumyldiphenylamine, and N-cyclohexylthiophthalimide; said sulfur vulcanization accelerator is selected from at least one of dibenzothiazyl disulfide, 2-mercaptobenzoazole, N-oxydiethylene benzothiazole-2-sulfenamide, 4-morpholinyl-2-benzothiazole disulfide, tetramethylthiuram disulfide, tetramethylthiuram monosulfide, tetrabutylthiuram disulfide, zinc dibutyldithiocarbamate, thiocarbqamuy sulfenamide, N-cyclohexyl-2-benzothiazolesulfenamide, N-t-butyl-2-benzothiazole sulfenamide, and diphenylguanidine; and wherein said vulcanization retarder are N-nitrosodiphenylamine, N-cyclohexyl thiophthalimide, magnesium oxide, and N-(cyclohexylthio)-phthalimide;

(B) a sulfur vulcanization accelerator selected from at least one of dibenzothiazyl disulfide; 2-mercaptobenzoazole; N-oxydiethylene benzothiazole-2-sulfenamide; 4-morpholinyl-2-benzothiazole disulfide; tetramethylthiuram disulfide; and tetramethylthiuram monosulfide; zinc dibutyldithiocarbamate, thiocarbqamuy sulfenamide, N-cyclohexyl-2-benzothiazolesulfenamide, N-t-butyl-2-benzothiazole sulfenamide, and diphenylguanidine; and/or

(C) a vulcanization retarder selected from at least one of N-nitrosodiphenylamine; N-cyclohexyl thiophthalimide, magnesium oxide and N-(cyclohexylthio)-phthalimide.

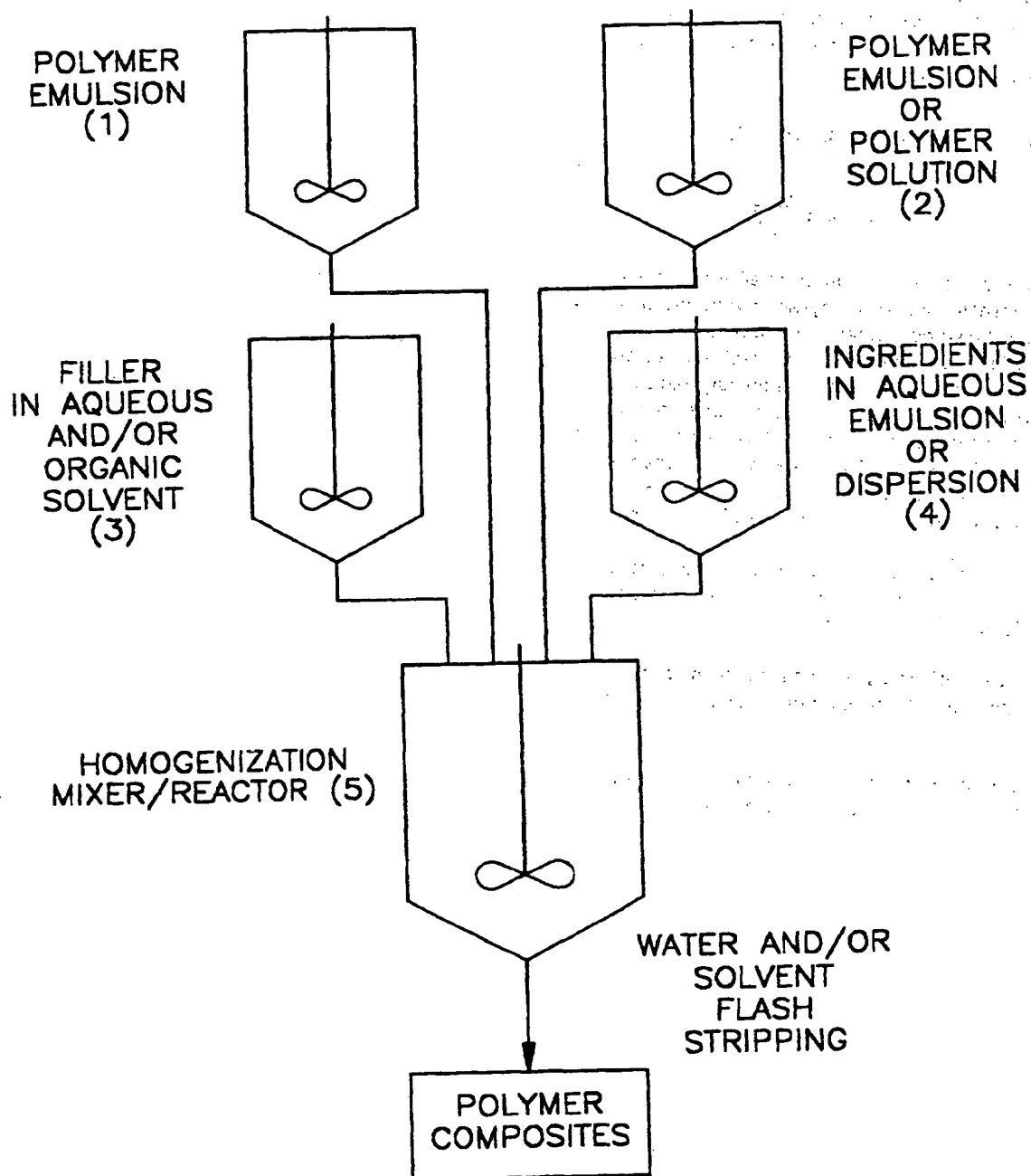
7. The process of claim 1 **characterized in that** additional ingredients are blended with said elastomer emulsion comprised of zinc oxide, stearic acid and sulfur and wherein said recovered rubber compos-

ite is sulfur vulcanized at a temperatur in a range of 150°C to 180°C; and wherein said filler is an amorphous silica which is pre-treated, prior blending with said aqueous emulsion of elastomer(s), by reacting said silica with an organosilane of the general formula (I) and/or II:



wherein R is the same or different alkyl radical selected from at least one of ethyl and methyl radicals, preferably the same radicals and preferably an ethyl radical; R' is the same or different radical selected from at least one of ethyl, propyl and butyl radicals, preferably the same radical and preferably a propyl radical; and n is a value from 2 to 6 with an average of from 2 to 2.6 or from 3.5 to 4 and Z is independently selected from -SH, -NH<sub>2</sub>, Acrylate, R'-NH-R', epoxy, -SCN, -NCO, -Sn-NH-R'-Si-(OR)<sub>3</sub> groups.

8. A composition **characterized by** being comprised of an elastomer composition prepared according to any of the preceding claims.
9. A tire **characterized by** having at least one component comprised of the elastomer composition of claim 8.
10. A tire **characterized by** having a tread comprised of the elastomer composition of claim 8.



# **POLYMER COMPOSITES FROM AQUEOUS EMULSION/DISPERSION MIXING**

**FIG-1**

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